HYDRATE CHEMISTRY VOLUME 2

ADVANCES IN CARBOHYDRATE CHEMISTRY

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EDITORS' PREFACE

The first volume of this series was published during the war and contained chapters written only by American authors. In this second volume we are especially pleased to be able to present several articles from the English school of carbohydrate chemists and one from France, thus making the "Advances" international in scope. Dr. Stanley Peat of Birmingham University, England, has been of great help in making arrangements for these and future articles. As communications between countries become facilitated, we hope to increase the number of countries that the participating authors represent.

We wish again to extend a cordial invitation to carbohydrate chemists to suggest topics in need of review and to suggest any way in which our contributions to the field of carbohydrates may be improved.

Dr. L. T. Capell has again compiled the subject index. The editorial assistance rendered by Edgar E. Dickey and Mary Grace Blair has been greatly appreciated. Dr. Claude S. Hudson has given invaluable aid in the editing of this and the preceding volume.

The journal abbreviations used are those employed by Chemical Abstracts. Unless otherwise noted, all temperature values are expressed in centigrade units.

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CONTENTS

Analogs of Ascorbic Acid

By F. Smith, *The University, Birmingham, England*

The Chemistry of Mucopolysaccharides and Mucoproteins

BY M. STACEY, *The University, Birmingham, England*

Bacterial Polysaccharides

By Taylor H. Evans and Harold Hibbert, *Research Laboratories, Dominion Rubber Co., Ltd., Guelph, Ontario, Canada, and McGill University, Montreal, Quebec, Canada*

The Chemistry of Pectic Materials

By E. L. Hirst and J. K. N. Jones, *The University, Manchester, England*

The Polyfructosans and Difructose Anhydrides

By Emma J. McDonald, *National Bureau of Standards, Washington, D. C.*

Cellulose Ethers of Industrial Significance

By Joseph F. Haskins, *Department of Chemistry, The Ohio State University, Columbus, Ohio*

MELEZITOSE AND TURANOSE

By C. S. Hudson

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Contents

Introduction

The modern scientific record concerning melezitose begins in the year 1822, and it originates in France. The growth of our information regarding this sugar has revealed so extensive an occurrence of it in nature that it is no longer a scientific curiosity, as it was in earlier years. It has been found in the exudations from so many plants of widely different botanical classifications that it should be recognized as one of the more important and widely distributed sugars of nature. In some localities such plant exudations are collected by bees when floral nectar is scarce; in consequence, melezitose is often found in so-called "honeydew" honey, which can become a firm magma as a result of the crystallization of this sugar. In recent years the professional apiarists in some localities of the Eastern United States have become quite familiar with the recondite name of this sugar; to them "melezitose honey" means trouble, because the sugar crystallizes so rapidly in the comb that it interferes with their centrifuging process for making "extracted" liquid honey. It is difficult to believe that prehistoric man was not acquainted with crystalline melezitose in places where it is often abundant; he did not need to invent the art of crystallizing it, as was the case with sucrose.[1] In some localities of British Columbia the bears know melezitose; surely early man of that section did not overlook it. In a vast desert region of Asia an exudation from a low bush named "camel's thorn" (*Alhagi camelorum* or *maurorum*) is known to have been an article of extensive commerce for at least a thousand years; this dried "manna" sometimes contains much crystalline melezitose. Probably the only crystalline sugars that were known to prehistoric man were melezitose and D-glucose, the latter often being present in crystallized honey and on the surface of raisins and some other dried fruits.

I. The Larch Manna of Briancon

A memoir was published in 1822 by Moringlane, Duponchel and Bonastre[2] in response to a question which had been proposed by the Paris Society of Pharmacy for investigation, the subject of the proposal being "to establish a precise distinction among the diverse natural products of the *Terebinthaceae* and the *Coniferae*." The twenty-page memoir is devoted principally to the description of the characteristic

(1) E. O. Von Lippmann, "Geschichte des Zuckers," Max Hesse's Verlag, Leipzig (1890). The art of crystallizing sucrose seems to have had its crude beginning in India at some period between 300 and 600 A.D., probably nearer the later date, but sirups from the juices of sugar canes were doubtless made in far earlier times.

(2) Moringlane, Duponchel and Bonastre, *J. Pharm.*, [2] 8, 329 (1822).

properties of the turpentines and resins of commerce, but in the section relating to the products from the larch tree (*Larix europaea* DC.), the authors describe, in addition to Venice turpentine, two substances which are soluble in water and therefore are not of a resinous nature. One of these is a gum which was known in Russian pharmacies as Orembourg gum and was considered to resemble gum arabic; the other is a kind of manna that was found at times on larch trees in France and was commonly known as "manna of Briançon," from the locality where it had become recognized. They describe the manna as follows (in translation):

"It is a secretion which forms on the young larch trees, or better even upon the older ones where it is present on the twigs of the new growth. The secretion is the more abundant if the summer is dry and hot, cold winds being unfavorable for it. It is collected in the very early morning when there is still dew, because it disappears completely when the sun has risen. There are years when it is not purchasable even at an offering of twenty-four francs an ounce, but during severe droughts it is obtainable from the children of the shepherds. Occasionally some branches of a larch tree are so charged with the manna that they appear as though snow had fallen upon them. The secretion consists of small sticky whitish grains, of dull sweetish flavor; the shepherds find them to be purgative but this property is less active than in the case of the manna of the ash tree."

Eleven years later the inquiring pharmacist Bonastre[3] resumed the study of the sample of Briançon manna which he had procured in 1822, and he now says that the manna is not an article of commerce but that (in translation) "nevertheless, as an object of natural history, of pharmaceutical and medical interest, it is not to be disdained. Its formation on a tree of the family of the conifers, which furnishes turpentine in abundance, its prompt appearance at some period which is not fully predictable, and its sudden disappearance under certain solar and atmospheric influences, naturally make it a subject worthy of study." He determined that the principal component of Briançon manna is a substance which may be recrystallized from water and is different from the well known mannitol [designated D-mannitol later by Emil Fischer] of Calabrian manna, the manna of the ash tree (*Fraxinus Ornus*, L.). He describes the crystals from the Briançon manna as growing from concentrated aqueous solution in the form of "square platelets arranged about a common center, widening as they diverge."

Twenty-three years elapsed after the studies of Bonastre before this

(3) Bonastre, *J. Pharm.*, [2] 19, 443, 626 (1833).

curious manna of Briançon attracted attention again. Berthelot,[4] in 1856, obtained a small sample of it (two grams), with which he was able to make a preliminary study of its crystalline component that Bonastre had described. This pure crystalline substance seemed to be a nonreducing compound sugar, as shown by its analysis and its reduction of Fehling solution after acid hydrolysis. It was difficultly fermentable by yeast but fermented readily after hydrolysis. It resembled sucrose but differed by its crystal form and its much larger rotation. Three years later Berthelot succeeded in obtaining a sufficient quantity of Briançon manna to enable him to characterize the saccharine component more specifically; on the basis of these data he definitely classified the pure crystalline substance as a new compound sugar, to which he gave the name melezitose (French *le mélèze*, the larch tree[5]). The sugar contained somewhat more than 4% water of crystallization, the exact proportion being uncertain because of efflorescence. After its acid hydrolysis, D-glucose was identified. The crystallization of melezitose in square plates, which Bonastre had mentioned, was confirmed; its specific rotation, as anhydrous melezitose, for the "teinte de passage" was found to be $[\alpha]_j$ +94.1° in water, a value which corresponds to about $[\alpha]_D$ +88.4°.

II. The Alhagi Manna (Turanjabine)

In 1870, Messrs. Allen and Hanburys, pharmacists of London, presented to Berthelot a sample of a manna which had been sent from Lahore by Dr. Burton Brown; it was described as an exudation from a spiny bush, *Alhagi maurorum*, belonging to the *Leguminosae*. This manna was said to be very abundant in Persia, where it was used as a purgative and even as a food under the name "taranjbin." The manna was well known to Avicenna and other writers of the Middle Ages; references to them may be found in Von Lippmann's "Geschichte des Zuckers,"

(4) M. Berthelot, *Ann. chim. phys.*, [3] 46, 66 (1856); 55, 282 (1859). He mentions that the former use of the manna in pharmacy had ceased and that it was not an article of commerce in 1859. Arnhart (ref. 22) records that the Paris tariff regulations of the year 1542 mention the *manna Brianzona* or *Briantica*. Nicholas Lemery's Dictionaire des Drogues, third edition, p. 298 (Amsterdam, 1716) carries the following statement: "Il découle des grosses branches des Melezes qui croissent en grande quantité dans le haut Dauphiné, principalement aux environs de Briançon, une manne blanche et seche qu'on appelle en Latin *Manna laricea* et en Francois *Manne de Briançon*. Elle est purgative."

(5) The Latin classical name of the tree was *larix*, but the authorities have not found any historical relationship of the French to the Latin name; they classify *mélèze* as originating in Alpine patois. The word *larix* occurs many times in Pliny's Natural History.